# CORRELATION OF DIELECTRIC AND CALORIMETRIC CHARACTERISTICS FOR AN AMORPHOUS DONOR-ACCEPTOR COPOLYMER

Valentina Elena MUSTEATA,[*] Vasile Cristian GRIGORAS and Virgil BARBOIU

"Petru Poni" Institute of Macromolecular Chemistry, 41 A Grigore Ghica Vodă Alley, 700487, Iaşi, Roumania

Dielectric and calorimetric studies were performed on a series of copolymers with different ratio of electron acceptor (3,5-dinitrobenzoil) and electron donor (phenothiazinyl) side groups. Both the calorimetric glass transition and α relaxation temperature corresponding to dynamic glass transition presented a positive deviation from the weighted average of the homopolymers, correlated with the density of donor-acceptor interactions. For the frequency dependence of α temperature an exponential expression was proposed, $T_\alpha \sim f^{0.093}$, and α temperature which would correspond to static electric field was determined and compared with glass transition. From the analysis of isothermal frequency data, the Vogel temperature at which the segmental movement ceases, equivalent to the Kauzmann temperature, was determined and was found to exhibit a relative maximum for the equimolar composition.
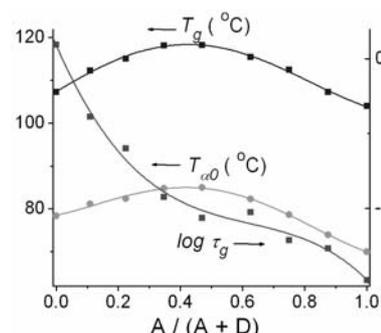
INTRODUCTION

The most investigated aspects in the dielectric relaxation spectra of polymers are those regarding the glass-rubber transition. Although widely used in the processing of materials and intensively studied, the glass transition (g. t.) still remains a mysterious phenomenon,[1] without satisfactory microscopic and theoretic explanations, but with an impressive number of questions persisting in the field of glassy material dynamics.[2]

A semiempirical relation, the VFTH (Vogel-Fulcher-Tammann-Hesse)[3-5] equation, with the form

$$\log \tau / \tau_0 = B / (T - T_0) \qquad (1)$$

is still everywhere used for the temperature dependence of the dielectric α-relaxation time, τ,

when $T > T_g$, including the domain near T_g, although these equations perform best for polymers which show small deviations from Arrhenius behavior, particularly for $T > T_g + 50$ K.[2,6] Known as the Vogel-Fulcher temperature, the temperature T_0 is considered as the configurational ground-state temperature, *i.e.* a hypothetical kinetic temperature associated with zero cooperative mobility. Sometimes a parallel is made between T_0 and the Kauzmann temperature that is considered both a hypothetical thermodynamic temperature and an ideal g. t. temperature.

Linear dependences between conveniently formulated parameters as functions of relaxation time or rate and of temperature have been sought in non-Arrhenius ($T < 1.3\ T_g$) regions in order to facilitate extrapolations for $T \rightarrow T_g$.[6] As shown

further on, we used a VFTH expression with $T_0 = 0.77$ T_g which was proved by Liu *et al.*[7] that generates linear plots for a series of amorphous polymers over the non-Arrhenius region ($T < 1.3$ T_g).

The present article displays a Dielectric Relaxation Spectroscopy (DRS) study carried out on a series of nine polymers containing similar electron-donor (ED) and electron-acceptor (EA) side groups in ratios ranging from the pure ED to the EA homopolymers, the rest of seven being random copolymers. The interacting groups, phenothiazinyl and 3,5-dinitrobenzoyl, are distanced from the methacrylic backone by sufficiently long spacers so to assure their free rotations (Scheme 1).
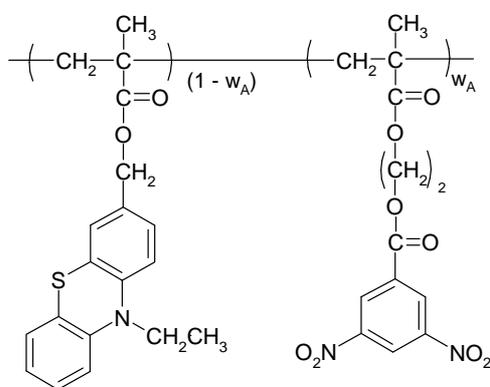
Scheme 1 – Chemical structure of the studied polymers.

Copolymers with similar structure were first reported by Simionescu, Percec and Natansohn,[8-10] and their initial studies were referred to synthesis and donor-acceptor (DA) interactions in solution. Such interactions were later evidenced in solid state by photoconduction,[11-13] DSC[14-17] and ^{13}C-NMR spectra.[14] Therefore the existence of DA interactions for the copolymers in Scheme 1 was an expected property. Similar to other related polymers,[14-17] these copolymers show positive deviation of the T_g values from the weighted average of the homopolymers.[18] This interesting characteristic will be referred in the present study relative to the dielectric α-relaxation. It can be explained that the DA interactions exert a hindering effect on the molecular dynamics,[19] *e.g.* similarly to that of crosslinks.[20]

RESULTS

1. Relevant characteristics of the polymers studied

A series of characteristics were already communicated elsewhere.[19] Thus it has been shown that all polymers in the series have predominant syndiotactic configuration and the copolymers are characterized by a random sequence distribution which is supported by the equality between the molar fractions of comonomers in the copolymers, w_A, and in the copolymerization medium, W_A (Table 1). It is to be mentioned that the values of molecular mass were found to be higher than 30 kDa that is considered the low limit from which the g. t. temperature is not longer dependent on the polymer weight.[21]

The DSC determined T_g shows a weak maximum placed at $w_A = 0.4 \div 0.5$. Its amplitude is only $3 \div 4\%$ of the homopolymer values. Such a dependence can be explained starting from the Fox-Loshaek equation[21] where the crosslink density is replaced with the concentration of the DA associations.[19] Further on, the notation T_g will be used for T_{gDSC}.

Table 1

Data about composition and glass transition of the studied polymers

Sample	W_A	w_A	T_{gDSC} [19]	
			(°C)	(K)
P1	0.0	0.0	107 .3	380.4
P2	0.125	0.11	112.3	385.4
P3	0.25	0.22	115.1	388.2
P4	0.375	0.38	118.2	391.3
P5	0.5	0.47	118.3	391.4
P6	0.625	0.62	115.5	388.6
P7	0.75	0.75	112.5	385.6
P8	0.875	0.87	107.3	380.4
P9	1.0	1.0	104.0	377.1

2. Isochronal dielectric behavior

The temperature dependence of dielectric loss for different fixed frequencies is represented in Fig. 1.A. for P7 copolymer. In the negative temperature region a peak with small amplitude and large width appears. It is correlated for other polymethacrylates with the rotation of side group and named β relaxation.[22,23] At temperatures exceeding the calorimetric glass transition there is α relaxation peak, overlapped for the lower frequencies by the conductivity losses. As typical for dielectric relaxations both processes shift to higher temperatures when the electric field frequency increases. All the polymers present these dielectric features, and only α-relaxation will be further on considered, this process being associated with the much studied glass transition phenomenon. Fig. 1.B. shows extended α-relaxation peaks (+100 to +165 °C) for all the polymers a intermediate

frequency,1 kH, at which the conductivity effects are negligible.

About the effect of the fraction of acceptor units, w_A, on the temperature T_α, which corresponds to the α peak maximum, one observes that this temperature slightly increases with w_A for $w_A < 0.5$, and decreases with w_A when $w_A > 0.5$. This means that the temperature T_α is maximum at about $w_A = 0.5$. Because the conductivity losses overlap the α relaxation peak on the high temperature side and at low frequencies, the values of T_α were determined by decreasing the conductivity effects with a procedure reported previously.[24] Fig. 2 presents the composition dependence of T_α at various frequencies. One observes the presence of maxima situated at $w_A = 0.4 \div 0.5$. Another observation is that T_α is lower than T_{gDSC} when $w_A > 0.5$ and $f \le 1$ Hz.
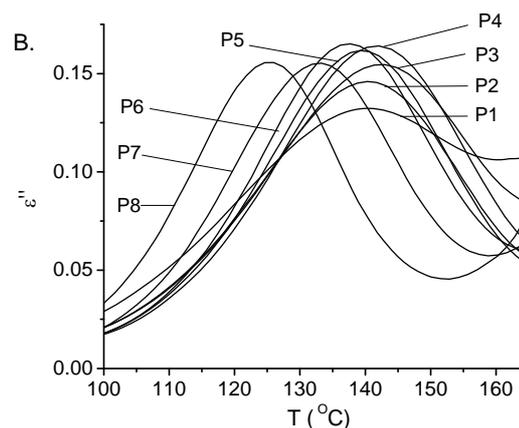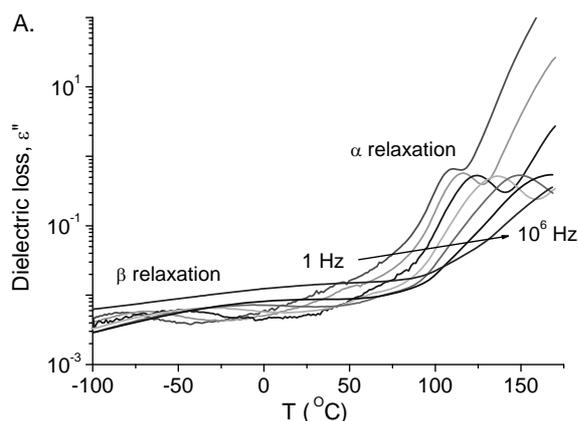

Fig. 1. A – Temperature dependence of ε" at several frecvencies in the 1 to 10^6 Hz interval for P7 copolymer.
B. Temperature dependence of dielectric loss at 1 kHz for all the polymers in α-relaxation temperature domain.
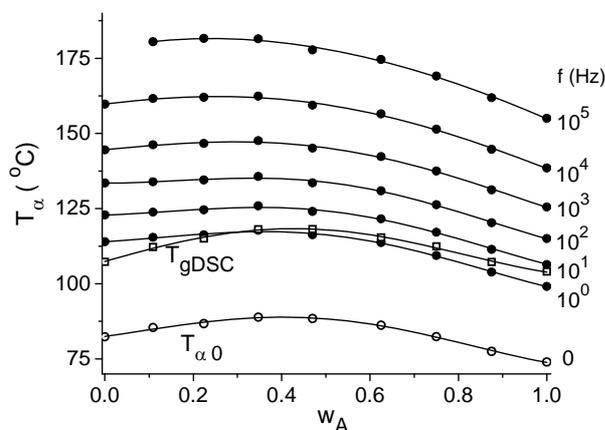

Fig. 2 – T_α vs. w_A plots obtained from ε'' thermograms for the electric field frequency, f, changed in decades (●).Open squares (□) and circles (○) are used for T_{gDSC} and $T_{\alpha 0}$.
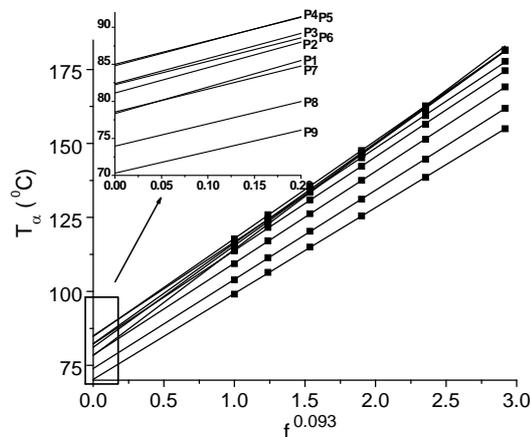
Fig. 3 – Plots of T_α versus $f^{0.093}$ to get the values $T_{\alpha 0}$ for each sample (Table 2).

Table 2

$T_{\alpha 0}$ and m values obtained by fitting equation (2) with $n = 0.093$ to measurements of T_{α} vs. f.

Sample	$T_{\alpha 0}$		m	$T_{\alpha 0}/T_g$
	(^{0}C)	(K)	(K/Hz^n)	
P1	78.35	351.49	35.85	0.924
P2	81.13	354.27	34.31	0.919
P3	82.41	355.55	33.92	0.916
P4	84.81	357.95	33.08	0.915
P5	85.01	358.15	31.72	0.915
P6	82.26	355.40	31.61	0.915
P7	78.57	351.71	31.01	0.912
P8	73.95	347.09	30.12	0.912
P9	70.03	343.44	29.02	0.910

The next step was to determine $T_{\alpha 0}$, that is the α-peak maximum temperature when $f \rightarrow 0$. So, T_{α} (f^n) dependences were searched, being found that the plots with equation

$$T_{\alpha} = T_{\alpha 0} + m f^n \qquad (2)$$

are straight lines when the exponent n takes values from 0.09 to 0.1. The plots in Fig. 3 were generated with $n = 0.093$ which is the mean of the values corresponding to minimum deviations from linearity for each sample in the series. These plots are given both for a wide frequency domain (0 - 200 kHz) and also for a very narrow one closed to $f = 0$, where the intercepts $T_{\alpha 0}$ can be better observed (inside figure). The values of $T_{\alpha 0}$ and m are given in Table 2.

3. Isothermal dielectric spectra

Fig. 4 illustrates the frequency dependence of dielectric losses ε" for the α-relaxation at two temperatures, 127 and 152 ^{0}C, situated close and well above to the glass transition domain of the sample. As expected, the *α*-peaks shift to higher frequencies when the temperature increases. When the difference ($T - T_g$) with $T > T_g$ is too small, the peaks for polymers with $w_A < 0.5$ are broad and affected by the dc conduction (Fig. 4A) which might cause some errors in the determination of relaxation time. On the other hand, when the recording temperature was sufficiently higher than T_g, the peak frequency, f_{α}, changed visibly with w_A,

even for $w_A < 0.5$ (Fig. 4B). However, the peak of P1 still remains rather deformed most probably due to the dc conduction effect. Due to this fact, the frequency f_{α} can not be directly measured near T_g for the samples with $w_A < 0.5$. So, the applied method was the calculus of relaxation time at T_g, τ_g, performed by the extrapolation of $\tau(T)$ dependences for $T = T_g$.

Fig. 5 shows the dependences resulted with the WinDeta - WinFit 3.2 Novocontrol software based on the HN equations (3) and (4) as well as corresponding fitting curves. The absence of some points in those graphics, mainly those corresponding to small w_A values and temperatures closed to T_g, is because the software fails to calculate when the α-relaxation signal is both too broad and too deformed. Using the coordinates of the points in Fig. 5, it was proved that the VFTH equation with $T_0 = 0.77 \, T_g$ is rather well followed, *i.e.* the plots are straight lines for both $T \geq 1.00 \, T_g$ (the samples P3 to P8) and $T \geq 1.06 \, T_g$ (the samples P1, P2 and P9) (Fig. 6). As mentioned before, a similar dependence was already reported by Liu et al.[7] for $T > 1.1 \, T_g$ by using data from various amorphous polymers. The cases with $T_0 = T_{\alpha 0}$ and $T_0 = 0.77 \, T_{\alpha 0}$ were then considered but the plots *log* τ versus $x = 1/(T - T_0)$ were much deviated from linearity (Fig. 7). The conclusion was that, except for the case $T_0 = 0.77 \, T_g$, the dependence of *log* τ on x is (i) more and more non-linear as the modulus difference $|T_g - T_0|$ is larger.
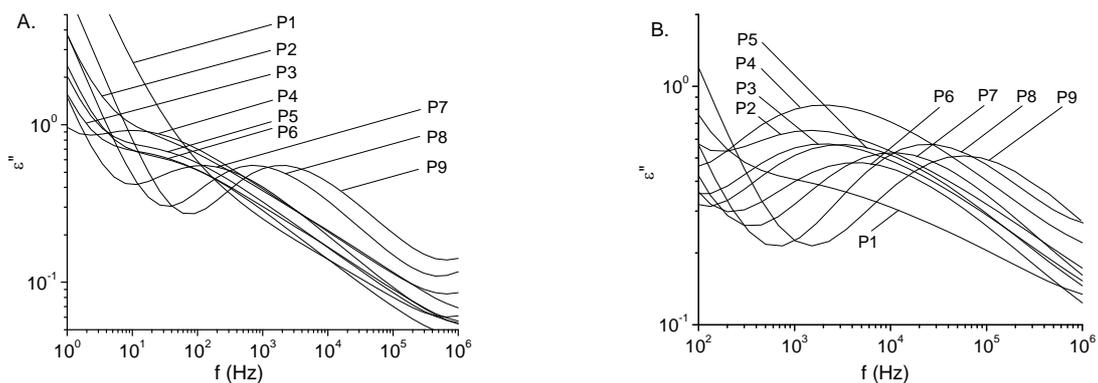
Fig. 4 – α-Relaxation peaks in ε'' spectra recorded at (A) 400 K (127 ^{0}C) and (B) 420 K (147 ^{0}C).
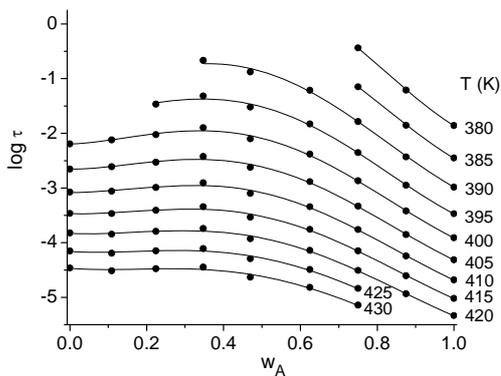

Fig. 5 – $log\ \tau$ versus w_A for temperatures from 380 to 430 K (full circles), and corresponding fitting curves.
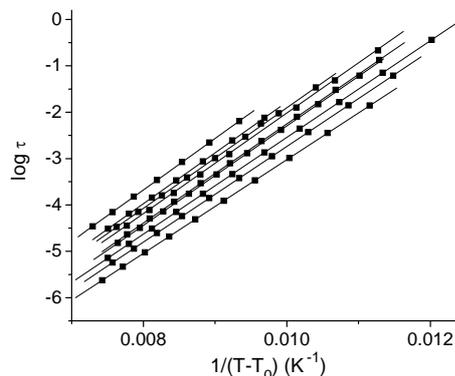
Fig. 6 – VFTH plots with $T_0 = 0.77\ T_g$ for the signal ε'' in α-relaxation range: experimental points ($\blacksquare$) and fitting linear dependences for each measured polymer.
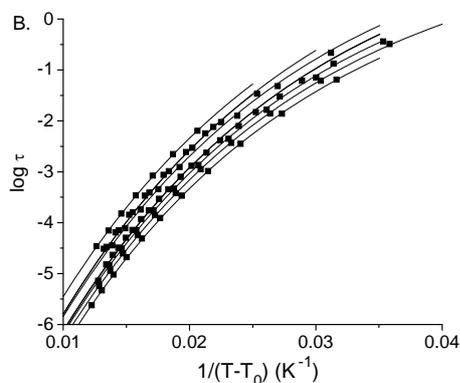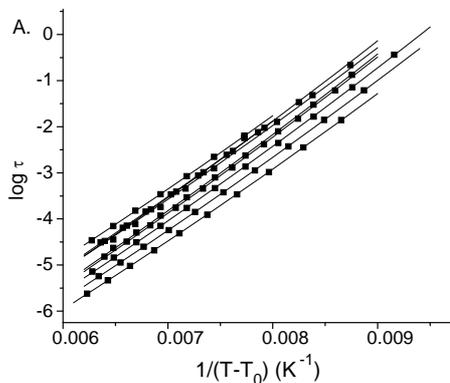

Fig. 7 – Plots $log\ \tau$ versus $x = 1/(T - T_0)$ for $T_0 = 0.77\ T_{\alpha0}$ (A) and $T_0 = T_{\alpha0}$ (B). From up to down the plots correspond to the polymers P1 to P9 with an inversion between P5 and P6. The corresponding fitting curves generated with functions of $a + b\ exp\ (p\ x)$ type with $p = 50$ (A) and $p = -50$ (B).

DISCUSSION

An interesting characteristic deduced and defined from the isochronal spectra was the temperature $T_{\alpha0}$, i.e. the limit of the temperature T_α when the electric field frequency tends to zero. The temperatures $T_{\alpha0}$ and T_g show similar polymer composition dependences, both of them reaching a maximum value for approximately equimolar composition (Fig. 2 and Table 2). Their values are close to each other, but they are not quite equal, the ratio $T_{\alpha0}\ /T_g$ being 0.917 $\pm$ 1% (Table 2). A possible question is "why the two temperatures are not equal if the both of them are referred to the same chain segmental motion". A possible cause could be related to the different heating rates used

for measurements, 10 K/min for T_g and 5 K/min for $T_{\alpha0}$, although the differences of about 33 K are too large for such an explanation.

An attempt to determine T_g at 5 K/min failed because the ΔCp steps were too small and wide for acceptable determination errors. As $T_{\alpha0} < T_g$, it results that the temperature $T_{\alpha0}$ would be closer than T_g to the calorimetric ideal g. t. temperature defined for the zero heating rate, T_{g0}. On the other hand, the identity between the cooperative motions characterized by the temperatures $T_{\alpha o}$ and T_{go} is uncertain so that such a problem still remains open.

Much consideration should be also given with regard to the isothermal spectra. Thus, it was confirmed that the Adam-Gibbs relationship[25], $T_0 = 0.77\ T_g$, leads to the most linear log τ versus $1/(T - T_0)$ plots, and this applies to all the samples in the series and even near T_g for the samples P4 to P8 ($w_A > 0.37$) (Figures 5 and 6). Therefore the temperature $0.77\ T_g$ could be considered as the Vogel-Fulcher temperature. On the other hand, the relation $T_{\alpha0} = 0.917\ T_g$ found for the polymer series P1 to P9 leads to another form of the Adam-Gibbs relation, namely $T_0 = (0.84 \pm 0.08)\ T_{\alpha0}$ which refers to a parameter also determinable, *i.e.* the temperature $T_{\alpha0}$.
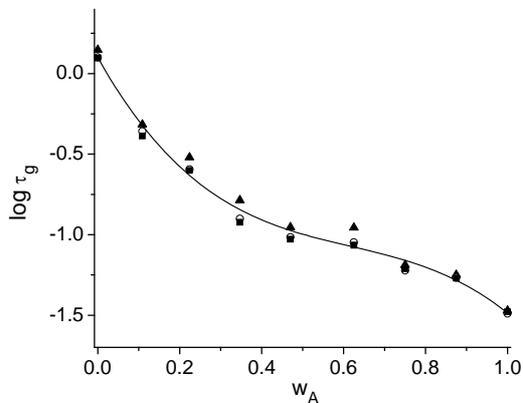

Fig. 8 – *log* τ_g versus w_A calculated according to three T_0 variants: $T_0 = 0.77\ T_g$ (■), $T_0 = 0.77\ T_{\alpha0}$ (○) and $T_0 = T_{\alpha0}$ (▲).

The plot in Fig. 8 illustrates the polymer composition dependence of *log* τ_g, where the relaxation time at T_g, τ_g, was calculated according VFTH equation, with T_0 taken as: $0.77 T_g$, $0.77 T_{\alpha0}$

and $T_{\alpha0}$. An unexpected continuous diminution of the τ_g with the amount of electron acceptor (EA) units was observed.

A plausible explanation for the polymer composition dependences of this characteristic would result assuming that the cooperative motion becomes lighter as the amount of EA units increases, what is equivalent with the diminution of the time τ_g when w_A increases. Another question would be why the cooperative motion would be faster in sequences with higher amount of electron acceptor units. An answer would be based on the inter and intramolecular interactions which are weaker between the EA groups than between the ED groups, the lasts being more sensitive at various physical and chemical factors.

EXPERIMENTAL

The copolymers and corresponding homopolymers reported in this study as well as their monomers were synthesized by methods detailed elsewhere.[26] Characteristic data such as the composition as the molar fraction of electron-acceptor 2-[(3,5-dinitrobenzoyl)oxyl] ethyl methacrylate units, w_A, and the glass transition temperature, T_g, are depicted in Table 1. The DSC thermograms, from which the values T_g were determined, were obtained from second heating scans with 10 K/min.[18]

Dielectric measurements in the frequency range from 1 to 10^6 Hz and temperatures comprised between -100 and +170 ^{0}C were carried out in a dry nitrogen atmosphere using a Novocontrol Concept 40 broadband dielectric spectrometer equipped with Novocontrol Quatro Cryosystem. For dielectric analysis each sample was prepared by pressing a pellet of pressed polymer between two circular stainless steel electrodes of 20 mm diameter, during the heating up to 170 ^{0}C. Three small strips of Kapton (DuPont product), with the surface of about 5% of the electrode aria and 125 μm thickness, were used as spacers.

The prepared samples were measured first at seven fixed frequencies, 1, 10^1, 10^2, 10^3, 10^4, 10^5 and 10^6 Hz, by sweeping the temperature from -100 to +170 ^{0}C with 5 ^{0}C/min heating rate, and second, by sweeping the frequency between 1 and 10^6 Hz at fixed temperatures, at 5 ^{0}C intervals, for the temperature above T_g, corresponding to α process. Each relaxation peak from frequency scan was described by fitting using Novocontrol software WinFit with a function composed from an exponential term for the conductivity effect and a Havriliak-Negami (HN) term[27] for α relaxation:

$$\varepsilon(\omega) = \varepsilon' - i\varepsilon'' = -i(\sigma_0 / \varepsilon_0 \omega)^n + \{\varepsilon_u + (\varepsilon_r - \varepsilon_u) / [1 + (i\omega\tau_{HN})^a]^b\} \tag{3}$$

$$\tau = \tau_{HN} \{\sin[\pi a b / (2 + 2b)] / \sin[\pi a / (2 + 2b)]\}^{1/a} \tag{4}$$

where σ_0 is the d.c. conductivity, n is an exponential factor, ε_0 is the permittivity of free space, $\Delta\varepsilon = \varepsilon_r - \varepsilon_u$ represents the

intensity of relaxation, with ε_r – the relaxed ($\omega \rightarrow 0$) and ε_u – the unrelaxed ($\omega \rightarrow \infty$) values of the dielectric constant for each

relaxation, $\omega = 2\pi f$ is the angular frequency, a and b are the broadening parameters, τ_{NH} is the HN relaxation time and τ is the actual relaxation time for the considered process.[28]

CONCLUSIONS

A series of amorphous methacrylate polymers containing phenothiazinyl and 3,5-dinitrobenzoyl side groups of different ratios were proved to be rather weak charge transfer complexes but with the glass transition temperature showing a maximum for the middle composition

A new characteristic was defined in the isochronal dielectric spectra of these polymers, *e.g.* the so-called α-relaxation temperature corresponding to the zero exciting frequency, $T_{\alpha 0}$. This temperature showed a polymer composition dependence similar to that of the temperature T_g, therefore with a weak maximum at the approximately equimolar composition.

The α-relaxation time at the glass transition temperature, τ_g, was determined from the VFTH plots which were rather linear for $T_0 = 0.77\ T_g$. Contrary to expectations, the polymer composition dependence of the time τ_g does not show maximum like the temperatures T_g and $T_{\alpha 0}$, but rapidly decreases when the fraction of electron acceptor units increases.

REFERENCES

1. J. Langer, *Physics Today,* **2007**, *60*, 8-9.
2. C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillian and S.W. Martin, *J. Appl. Phys.*, **2000**, *88*, 3133-3157.
3. H. Vogel, *Physik Z*, **1921**, *22*, 645-646.
4. G. S. Fulcher, *J. Am. Ceram. Soc.*, **1925**, *8*, 339-355 and 789-794.
5. G. Tammann and W. Hesse, *Z. Anorg. Allg. Chem.*, **1926**, *156*, 245-257.
6. K. Liedermann, *Colloid. Polym. Sci.*, **1996**, *274*, 20-26.
7. C.-Y. Liu, J. He, R. Keunings and C. Bailly, *Macromolecules*, **2006**, *39*, 8867-8869.
8. C. I. Simionescu, V. Percec and A. Natansohn, *Polymer*, **1980**, *21*, 417-422.
9. C. I. Simionescu, V. Percec and A. Natansohn, *Polym. Bull.*, **1980**, *2*, 57-61.
10. C. I. Siminonescu, V. Barboiu and M. Grigoras, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, **1985**, *22*, 693-711.
11. A. Natansohn, *J. Polym. Sci., Polym. Chem. Ed.*, **1984**, **22**, 3161-3171.
12. C. Simionescu, V. Barboiu and M. Grigoras, *Polym. Bull.*, **1983**, *9*, 577-581.
13. C. Simionescu, V. Barboiu and M. Grigoras, *Polym. Bull.*, **1984**, *11*, 545-550.
14. A. Simmons and A. Natansohn, *Macromolecules*, **1991**, *24*, 3651-3661.
15. H. A. Schneider and U. Epple, *Thermochim. Acta*, **1987**, *112*, 123-130.
16. H. A. Schneider, C. Simionescu and G. David, *Thermochim. Acta*, **1992**, *207*, 131-145.
17. U. Epple and H. A. Schneider, *Thermochim. Acta*, **1990**, *160*, 103-112.
18. V. C. Grigoras and A. G. Grigoras, *J. Therm. Anal. Calorim.*, **2011**, *103*, 661-668.
19. V. Barboiu, A. G. Grigoras, V. C. Grigoras and G. L. Ailiesei, *Rev. Roum. Chim.*, **2012**, *57*, 151-157.
20. J. K. W. Glatz-Reichenbach, L. J. Sorriero and J. J. Fitzgerald, *Macromolecules*, **1994**, *27*, 1338-1343.
21. T. Blythe and D. Bloor, "Electrical properties of polymers", Cambridge University Press, Ed. 2, Cambridge, 2005, p. 83-84.
22. M.T. Viciosa, N. Rouzé, M. Dionísio and J.L. Gómez-Ribelles, *Eur. Polym. J.*, **2007**, *43*, 1516-1529.
23. K. Schmidt-Rohr, A.S. Kulik, H.W. Beckham, A. Ohlemacher, U. Pawelzik, C. Boeffel and H.W. Spiess, *Macromolecules*, **1994**, *27*, 4733-4745.
24. V. E. Musteata and V. Barboiu, *J. Optoelectron. Adv. M.,* **2012**, *14*, 678-684.
25. G. Adam and J. H. Gibbs, *J. Chem. Phys.*, **1965**, *43*, 139-146.
26. C. I. Simionescu, E. Bicu, M. Grigoras and V. Barboiu, *Eur. Polym. J.*, **1984**, *20*, 1053-1056.
27. S. Havriliak and S. Negami, *J. Polym. Sci. Polym. Symp.*, **1966**, *14*, 99-117.
28. A. Schönhals and F. Kremer, "Analysis of dielectric spectra", in: F. Kremer and A. Schönhals (Eds.), "Broadband Dielectric Spectroscopy", Springer-Verlag, Berlin, 2003, p. 59-98.